

Microwave photocatalysis III. Transition metal ion-doped TiO₂ thin films on mercury electrodeless discharge lamps: preparation, characterization and their effect on the photocatalytic degradation of mono-chloroacetic acid and Rhodamine B

Hana Žabová and Vladimír Církva*

Abstract

BACKGROUND: Mercury electrodeless discharge lamps (Hg-EDLs) were used to generate UV radiation when exposed to a microwave field. EDLs were coated with doped TiO₂ in the form of thin films containing transition metal ions Mⁿ⁺ (M = Fe, Co, Ni, V, Cr, Mn, Zr, Ag). Photocatalytic degradation of mono-chloroacetic acid (MCAA) to HCl, CO₂, and H₂O, and decomposition of Rhodamine B on the thin films were investigated in detail.

RESULTS: Polycrystalline thin doped TiO₂ films were prepared by dip-coating of EDL via a sol-gel method using titanium *n*-butoxide, acetylacetonate, and a transition metal acetylacetonate. The films were characterized by Raman spectroscopy, UV/Vis absorption spectroscopy, X-ray photoelectron spectroscopy (XPS), electron microprobe analysis and by atomic force microscopy (AFM). The photocatalytic activity of doped TiO₂ films was monitored in the decomposition of Rhodamine B in water. Compared with the pure TiO₂ film, the UV/Vis spectra of V, Zr and Ag-doped TiO₂ showed significant absorption in the visible region, and hence the photocatalytic degradation of MCAA had increased. The best apparent degradation rate constant (0.0125 min⁻¹), which was higher than that on the pure TiO₂ film by a factor of 1.7, was obtained with the Ag(3%)/TiO₂ photocatalyst. The effect of doping level of vanadium acetylacetonate on the photocatalytic efficiency of the V-doped TiO₂ was determined.

CONCLUSIONS: Transition metal ion-doped TiO₂ thin films showed significant absorption in the visible region. The metal doped TiO₂ photocatalyst (with an appropriate amount of V, Zr and Ag) on the Hg-EDLs increased the degradation efficiency of MCAA in a microwave field.

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Keywords: microwave photocatalysis; transition metal ion-doped TiO₂ thin films; mercury electrodeless discharge lamp; mono-chloroacetic acid; Rhodamine B

INTRODUCTION

Titanium dioxide, also known as titania, is established as an effective photocatalyst and in the form of a thin film its attractive properties include high chemical and thermal stability, high refractive index, high absorbance in the ultraviolet spectral range, high catalytic activity and low cost. Due to its unique properties, titania may be used in many applications, such as wastewater treatment¹ or polluted air deodorization.² However, the use of TiO₂ is limited by its wide band gap (3.2 eV) and thus for photocatalytic activation only UV light below 387 nm can be utilized. This restricts the potential applicability since only approximately 3–5% of the solar light reaching the Earth's surface falls within the range of ultraviolet light due to filtering by the ozone layer. Therefore, a visible-light active TiO₂ could provide a promising way to improve the photoactivity of titania.³

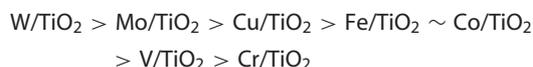
Irradiation of titania by light of energy higher than the band gap results in the formation of an excited electron (e⁻) and positive hole (h⁺) pair. These e⁻ and h⁺ reduce and oxidize chemical species on the photocatalyst surface.⁴ The most difficult issue is the rapid recombination of positive and negative charges, which must be overcome to achieve efficient photocatalysis. If the recombination occurs very quickly (mean lifetime of an electron-hole pair is about 30 ns) there is not sufficient time for other chemical reactions.⁵ A metal can capture the excited

* Correspondence to: Vladimír Církva, Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic, Rozvojová 135, 165 02 Prague 6, Czech Republic. E-mail: cirkva@icpf.cas.cz

Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic, Rozvojová 135, 165 02 Prague 6, Czech Republic

electrons from TiO₂ and leave the holes for the degradation reaction of organic compounds. Doping with transition metal ions allows light absorption to extend into the visible region. Also, metal ion doping can enhance interfacial charge-transfer reactions, thus increasing the photoreactivity of TiO₂.⁶

The sol-gel method has been widely used to prepare titania nanoparticles under controlled conditions. The integration of dopants into the sol during the gelation process facilitates direct interaction with TiO₂. Therefore, dopants could be incorporated into the titania lattice, resulting in materials with other optical and also catalytic properties.⁷ Di Paola *et al.*⁶ used a set of TiO₂ photocatalysts loaded with various transition metal ions (Co²⁺, Cr³⁺, Cu²⁺, Fe³⁺, Mo⁵⁺, V⁵⁺ and W⁶⁺) and tried to find a correlation between photocatalytic behavior and physicochemical properties of prepared samples. They reported a descending sequence of photocatalysts depending on their activities:



Chen *et al.*⁵ demonstrated that different ion doping exhibited complex effects on the characteristics of titania. Across the investigated ions (Zn²⁺, Fe³⁺, Cu²⁺, Co²⁺, Ni²⁺, Mn²⁺, V⁵⁺, Cr³⁺, Ni²⁺) doped TiO₂ has shown the highest photoactivity in the decoloring of methyl orange compared with bare TiO₂. Sharma *et al.*⁸ obtained similar results. They found that a Ni dopant (2–10 mol %) increased the activity of titania films in the case of methyl orange degradation. They also indicated that Ni ions suppress the grain growth of crystal in the TiO₂ film, revealed by atomic force microscopy (AFM) images. Wu *et al.*⁹ directed their research at developing a visible-light response catalyst via vanadium doping. They found that an increase in vanadium doping promoted particle growth and enhanced 'red-shift' in the UV/Vis absorption spectra. They concluded that vanadium was highly dispersed inside the titania structure using X-ray absorption spectroscopy (XAS) analysis and also evaluated the higher activity of V/TiO₂ by the degradation of crystal violet and methylene blue under visible light irradiation.

Another approach to the synthesis of a visible light active catalyst could be doping with non-metal atoms, such as carbon, nitrogen, and sulfur. Yang *et al.*¹⁰ synthesized a carbon doped TiO₂ and C- and V-doped TiO₂ by the sol-gel process. Both the catalysts showed high activity under visible light for acetaldehyde degradation. Moreover, the doped carbon increased the surface area and improved the dispersion of vanadium. Matsumoto *et al.*¹¹ prepared a nitrogen-doped titania from a layered titania/isostearate nanocomposite.

Recent papers^{12–17} have demonstrated outstanding improvement of the degradative efficiency by coupling microwave (MW) radiation with electrodeless discharge lamps (EDLs) for the photocatalytic degradation of various compounds (Rhodamine B,¹² atrazine,¹³ brilliant red X-3B,¹⁴ methylene blue,¹⁵ 4-chlorophenol,¹⁶ and 2,4-dichlorophenoxyacetic acid¹⁷). However, these experiments were carried out in an aqueous TiO₂ dispersion (slurry).

We previously reported^{18,19} the effect of operational parameters (number of coating cycles for EDL, number of titania-coated EDLs, light intensity, initial pH value, H₂O₂ dosage, flow rate, reaction temperature, and air bubbling) on the photocatalytic degradation of mono-chloroacetic acid (MCAA) to HCl, CO₂, and H₂O, on thin titania-coated EDLs in a batch MW photocatalytic reactor and in a continuous-flow MW reactor. In the present research a

number of transition metal ion Mⁿ⁺ (M = Fe, Co, Ni, V, Cr, Mn, Zr, Ag) doped titania thin films were prepared by the sol-gel method using titanium *n*-butoxide, acetylacetone, and transition metal acetylacetonate. Microwave powered mercury EDLs were coated with thin films of doped TiO₂. The enhanced photocatalytic degradation of mono-chloroacetic acid (MCAA) to HCl, CO₂, and H₂O, and decomposition of Rhodamine B as model reactions of organic pollutants were studied.

MATERIALS AND METHODS

Chemicals

Titanium *n*-butoxide (97%), acetylacetone (99.5%), ethyl alcohol (99%) were used as received (Sigma-Aldrich, Prague, CR) for the photocatalyst preparation. Iron(III) acetylacetonate (99.9%), cobalt(III) acetylacetonate (99.99%), nickel(II) acetylacetonate (95%), vanadyl acetylacetonate (98%), chromium(III) acetylacetonate (99.99%), manganese(II) acetylacetonate (99.99%), zirconium(IV) acetylacetonate (98%) and silver acetylacetonate (98%) (Sigma-Aldrich) were used as obtained for preparation of doped titania photocatalysts. Mono-chloroacetic acid (99%) and Rhodamine B were used as received (Lachema, Brno, CR) for the photocatalytic experiments. All solutions were prepared using distilled water (conductivity 1 μS cm⁻¹). Mercury (99.9999%, electronic grade) was used as obtained (from Sigma-Aldrich) for the EDLs preparation as well as argon (5.0 grade) purchased from Linde Technoplyn (Prague, Czech Republic).

Preparation of EDLs and spectral measurements

The vacuum system pattern for the preparation of titania-coated EDLs on Pyrex glass was described elsewhere.²⁰ The lamp length was 50 mm (diameter 20 mm). Spectral measurements of prepared lamps (light intensity in μW cm⁻² for the 366 nm line of mercury) were carried out using a spectrometer USB2000 with an optical fiber probe and operating software package OOIrрад-C (Ocean Optics, Dunedin, FL, USA).²⁰

Preparation of the transition metal ion-doped TiO₂ thin films

The TiO₂ photocatalyst was prepared using a sol-gel method. Titanium *n*-butoxide, Ti(OBu)₄, (10 mL) was dissolved in acetylacetone (acac) and used as a molecular precursor of TiO₂. The resulting reaction originated a solution, into which the solvent ethyl alcohol (EtOH) was added gradually. The volume ratio of these reactants was 1 : 1 : 1 [Ti(OBu)₄ : acac : EtOH]. Water used for hydrolysis was added dropwise under mechanical stirring at the molar ratio Ti(OBu)₄ : H₂O = 0.1. For doped TiO₂ photocatalysts, the synthetic procedure was the same as described above. The appropriate amount (0.1–0.95 g) of metal acetylacetonate was dissolved in acetylacetone. The metal-doped titania is denoted in this paper as a transition metal(x%)/TiO₂ when the percentage ((w/w) metal/TiO₂) of an added transition metal acetylacetonate amount has to be specified. Doping is also expressed as at % (using an X-ray photoelectron spectroscopy (XPS) technique) with respect to Ti. All EDLs were thoroughly purified and dried.¹⁸ Coatings of EDLs were made in the dip-coating machine at a withdrawal rate 6 cm min⁻¹. The films were then dried at room temperature for 1 h and calcined at 500 °C for 2 h (heating rate 2 °C min⁻¹).

Characterization technique of the doped TiO₂ thin films

Raman spectra were recorded by means of a dispersive Raman spectrograph (Nicolet Almega XR, Thermo Scientific, USA) to

examine the crystallographic phase of prepared samples (laser wavelength 473 nm, laser power 100%, objective 50×, pinhole 100 μm). UV/Vis spectrophotometry (Helios Unicam, Cambridge, UK) was employed in the range 200 nm to 800 nm to detect absorption edges of the layers produced. XPS was employed to examine both the valence state and the surface stoichiometries of the prepared sol-gel layers (ESCA PROBE P photoelectron spectrometer, Omicron Nanotechnology Ltd., Taunusstein, Germany; pressure 10⁻¹⁰ mbar; monochromatic Al Kα X-ray source with energy of 1486.7 eV). Measured spectra were analysed using the CasaXPS program (Casa Software Ltd., Teignmouth, UK). Sample charging was eliminated by correcting the observed spectra for a C 1s binding energy value of 284.7 eV. AFM images of the films were obtained using an explorer (ThermoMicroscopes, Sunnyvale, USA) and then analyzed to estimate the relative surface roughness (rms).

Photocatalytic experiments and analysis

The photoreactivities of pristine and doped TiO₂ thin films under UV irradiation were quantified by the decoloring rate of Rhodamine B (RhB, C₂₈H₃₁ClN₂O₃, M_R = 479 g mol⁻¹). RhB is a reddish-violet powder that is highly soluble in water. The absorbance²¹ of RhB at wavelength of 553 nm is used as an indicator of the photoreactivity of TiO₂ samples. In this study, undoped and doped TiO₂ layers prepared on microscopic slides were put into 10 mL RhB with concentration 10⁻⁴ mol L⁻¹. This solution was irradiated in a cuvette (30 × 50 × 10 mm) by high-pressure mercury UV lamp (HQL 400 W; Osram, Munich, Germany) for 90 min. The resulting solution absorbance was measured by UV/Vis spectrometer (Helios γ; Thermo Electron Corporation; software Vision 32). The conversion (x) of RhB for the initial 90 min was used to quantify the photoreactivity of TiO₂ that was calculated using the following equation:

$$x = \frac{A_0 - A}{A_0} \times 100\% \quad (1)$$

where A₀ is the absorbance of RhB before irradiation and A is the absorbance of RhB after irradiation. This quick photoreactivity

test was used for all the prepared doped photocatalysts and then the most active layers were prepared on the surface of EDLs and used for the MW-assisted photocatalytic oxidation of monochloroacetic acid (MCAA). The experimental set-up for MW-assisted photocatalytic reactions was the same as the previous one (150 mL of an aqueous solution of MCAA, 0.1 mol L⁻¹).¹⁸ Samples of MCAA were analyzed at regular intervals (20 min) using a chloride ion-selective electrode (ISE; Chloride Flow Plus Combination, Sentek, Braitree, UK). ISE was connected to a digital pH/mV meter (inoLab Level 1; WTW, Weilheim, Germany) calibrated with NaCl.¹⁸

RESULTS AND DISCUSSION

Characteristics of pristine and doped TiO₂ layers

Raman spectroscopy studies revealed that films annealed at 500 °C have anatase structure and show almost all of the expected vibrational modes of anatase TiO₂ (A_{1g} + 2B_{1g} + 3E_g), correlating with previous literature on Raman analysis of TiO₂.²² Fig. 1 shows the Raman spectra of titania films for different dopants. The spectra of the undoped sample and all other doped samples were almost identical showing the anatase crystal phase. For example, peaks observed at 134, 187, 389, 509, and 631 cm⁻¹ were attributed to the anatase phase of Ag-doped TiO₂. The UV/Vis spectra of pure and doped titania layers were obtained by absorption spectroscopy. Representative examples are shown in Fig. 2. The changes in the spectra, compared with the undoped TiO₂, are due to charge transfer transitions from the metal dopant ion to Ti⁴⁺. The spectra of Zr, V and Ag-doped samples showed a slight shift to the visible region (absorption edge 410, 420 and 424 nm, respectively). Also Fe-doped-titania had a red-shift (405 nm). The spectra of Ni, Cr, Mn and Co-doped TiO₂ are the same as those of pure TiO₂ (365 nm) in absorption edges (386, 372, 369, and 368 nm, respectively). In this study, it appears that doping with these transition metal ions does not change the band structure. However, the extent of the absorption spectrum also depends on the amount of metal loading.⁹

XPS analyses were made for all prepared samples of doped TiO₂. In this study, the actual binding energy positions corresponding to

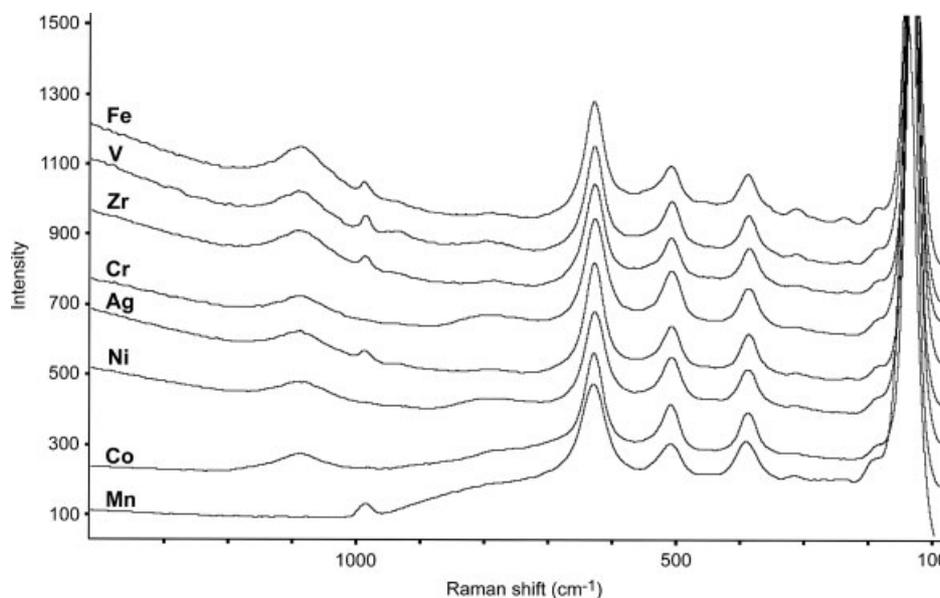


Figure 1. Raman spectra of various transition metal ion-doped TiO₂.

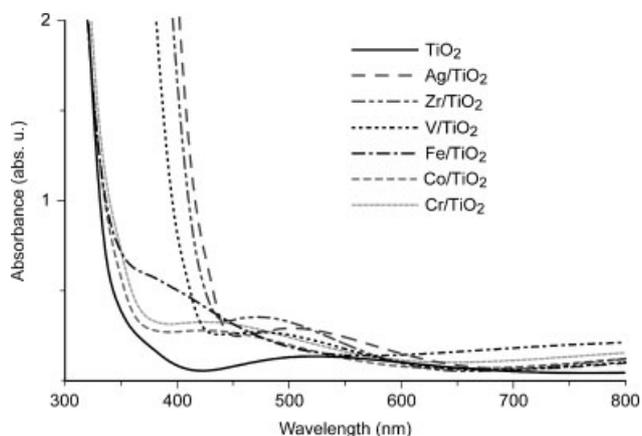


Figure 2. UV/Vis absorption spectra of pure and doped TiO₂ (3% (w/w) metal acac/TiO₂).

Ti 2p_{1/2} and Ti 2p_{3/2} lines for TiO₂ films were found at 465.1 eV and 458.0 eV (Fig. 3). These values agree well with reported XPS data and are known to be due to Ti⁴⁺ in pure anatase titania form.²³ The binding energy of Zr 3d_{5/2},²⁴ Ni 2p_{3/2},²⁵ and Fe 2p_{3/2}²⁶ lines (181.9, 854.8, and 711.0 eV, respectively) can be assigned to Zr⁴⁺, Ni²⁺, and Fe³⁺. Owing to the small binding energy difference (1.0 eV for 781.1 eV) and the band broadening caused by multiplet splitting, the presence of Co²⁺ or Co³⁺ (or both) cannot be established from the position of the Co 2p_{3/2} and 2p_{1/2} lines alone.²⁷ The core level of Mn 2p_{3/2} and 2p_{1/2} shows the binding

energy lines at 640.9 and 653.3 eV, respectively. These peaks with energy separation of 12.4 eV can be assigned to Mn²⁺.²⁸ The small peak of V 2p_{3/2} (516.0 eV) appeared as two shoulders (Fig. 3). The shoulder at a binding energy of 516.9 eV suggests V⁵⁺ species, whereas the shoulder at 516.3 eV can be assigned to V⁴⁺.^{10,29} Obviously, some V⁴⁺ ions were oxidized into V⁵⁺ in the preparation process, because vanadium existed only as V⁴⁺ in the precursor (as VO²⁺ vanadyl). The formation of V⁵⁺ possibly occurred during annealing. In the case of Cr/TiO₂ samples, the XPS shows two different Cr species, which can be assigned to the peak (2p_{3/2}) at 576.8 eV, corresponding to Cr³⁺, and the highest peak at 580.0 eV, corresponding to Cr⁶⁺.^{30,31} The binding energy of Ag 3d_{5/2} peak (367.3 eV) indicated that silver is in the metallic form Ag⁰ (Fig. 3).³² For the Ag⁺ ions spreading on the surface of titania under the action of heat can be reduced to Ag⁰ due to the high redox potential for the Ag⁺ ion. Also the Ag–O bonding is much weaker than Ti–O (or Ag–Ag) bonding and Ag has a higher surface free energy than TiO₂.^{33,34} The atomic percentage (at.%) of metals (for 3% (w/w) metal acac/TiO₂) ranging from 0.12 to 1.52 and the cation valency were obtained for the following metals: Ag⁰ (0.12), Fe³⁺ (0.35), Cr³⁺ (0.56), Mn²⁺ (0.99), Ni²⁺ (1.07), V⁴⁺ and V⁵⁺ (1.17), Co²⁺ and Co³⁺ (1.20), and Zr⁴⁺ (1.52).

AFM was used to characterize the uniformity and relative surface roughness of pure and doped titania films. As shown in Fig. 4, the pure TiO₂ film has a very smooth surface without any defects and its relative surface roughness is 0.41 nm. All other doped films have surface roughness in the range of 0.56–9.04 nm depending on the nature of the metal. The surface morphology of various films

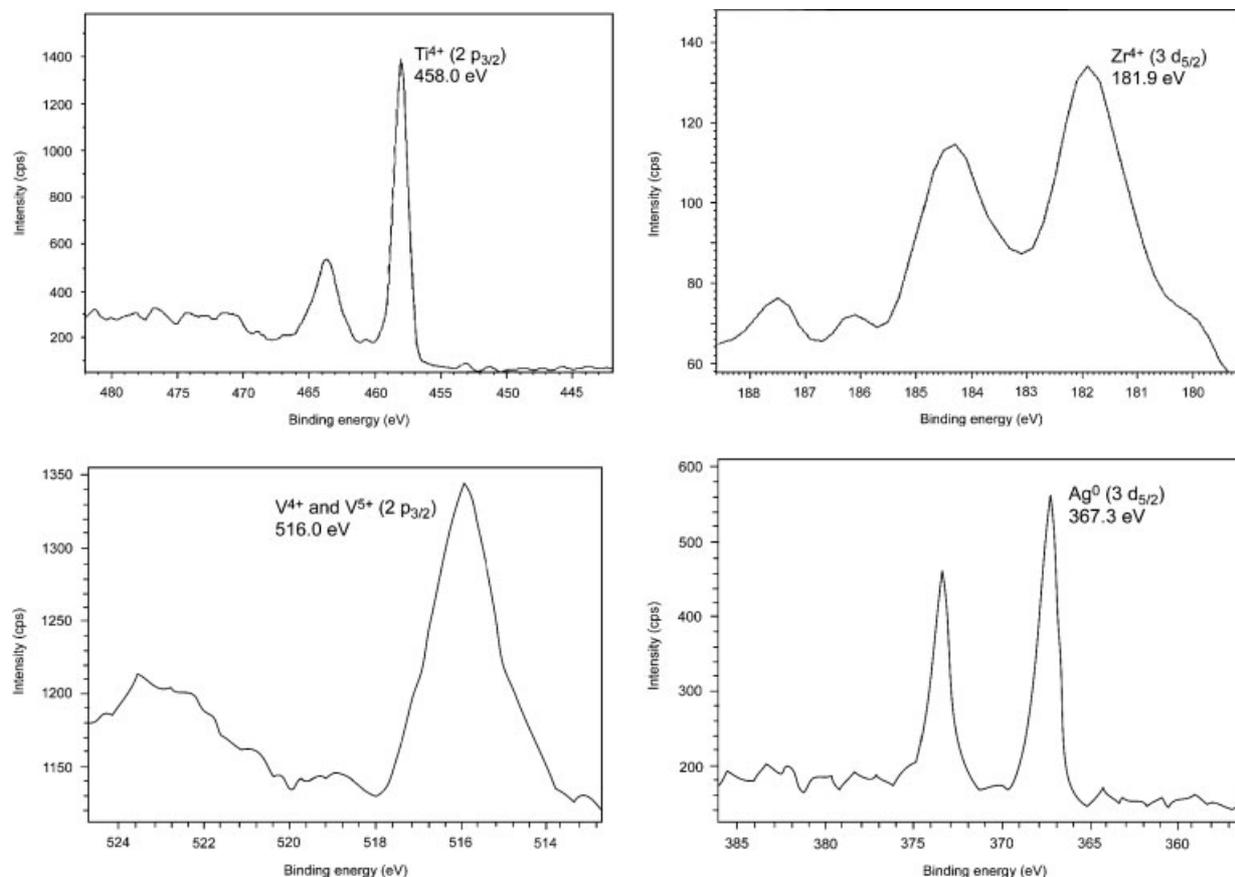


Figure 3. XPS spectra of the Ti 2p_{3/2}, Zr 3d_{5/2}, V 2p_{3/2}, and Ag 3d_{5/2} region for the surface of TiO₂ thin films.

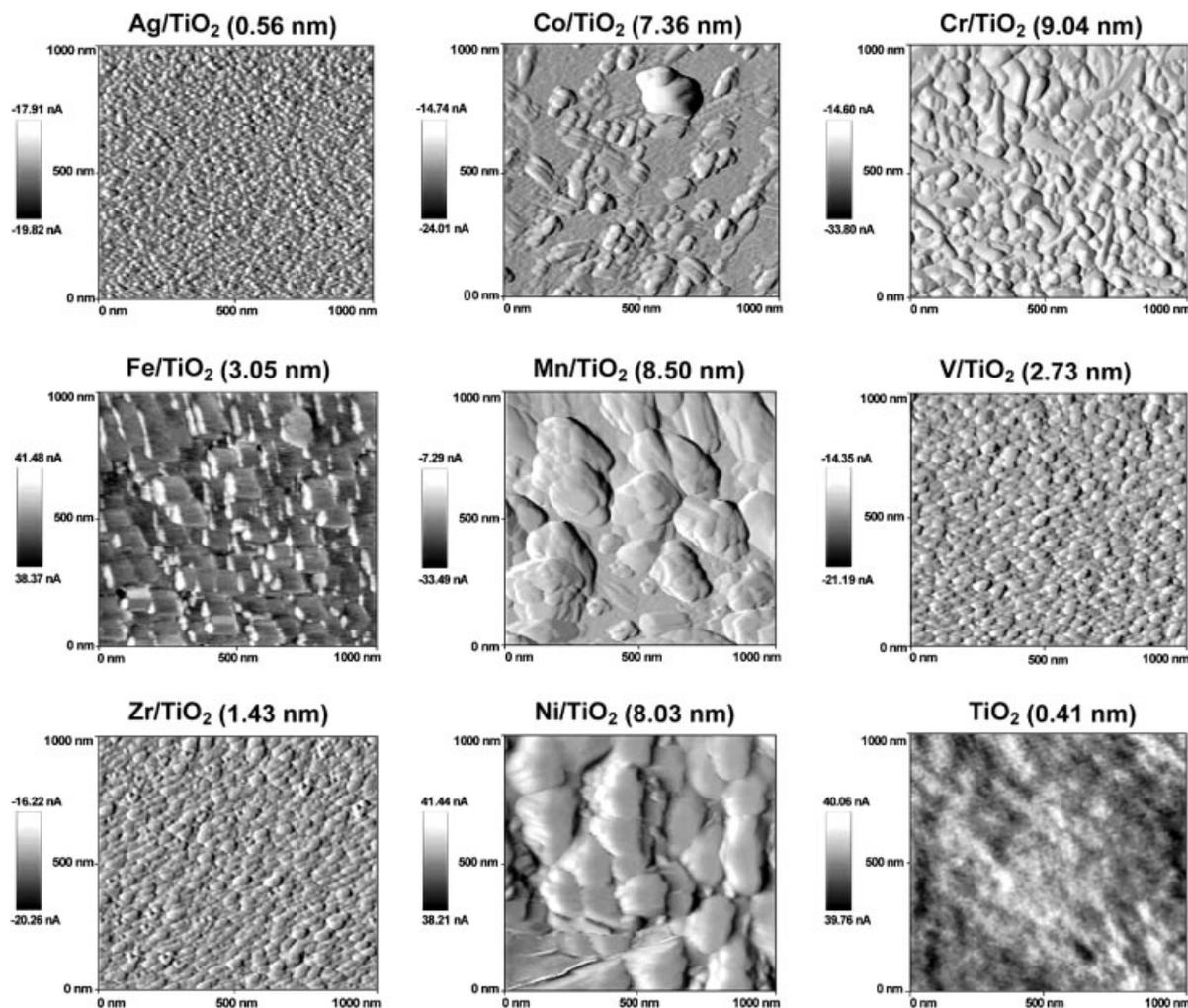


Figure 4. AFM images of prepared layers with their relative surface roughness (3% (w/w) metal acac/TiO₂).

Table 1. Photodecomposition of Rhodamine B (RhB) with initial concentration 10⁻⁴ mol L⁻¹ in 90 min on transition metal doped titania films (%(w/w) metal acac/TiO₂)

Catalyst	RhB apparent rate constant k_{app} ($R^2 \geq 0.99$) (min ⁻¹)	Conversion (%)
TiO ₂	0.0074	41
Ag(1%)/TiO ₂	0.0087	54
Ag(3%)/TiO ₂	0.0125	61
Ag(5%)/TiO ₂	0.0085	53
Zr(1%)/TiO ₂	0.0097	58
Zr(3%)/TiO ₂	0.0119	59
Zr(5%)/TiO ₂	0.0079	46
V(1%)/TiO ₂	0.0047	34
V(3%)/TiO ₂	0.0076	42
V(5%)/TiO ₂	0.0079	46
V(9%)/TiO ₂	0.0024	19
Fe(3%)/TiO ₂	0.0061	36
Ni(3%)/TiO ₂	0.0059	34
Co(3%)/TiO ₂	0.0053	31
Mn(3%)/TiO ₂	0.0042	25
Cr(3%)/TiO ₂	0.0038	21

obtained by AFM corresponds with the results for photocatalytic activity (see Table 1).

Effect of metal ion doping on the photocatalytic activity of TiO₂ films

The photocatalytic decomposition of organic pollutants in water generally follows the Langmuir–Hinshelwood mechanism:³⁵

$$r = \frac{kKc}{1 + Kc} \quad (2)$$

where r is the photocatalytic reaction rate (mol L⁻¹ min⁻¹), k is the photocatalysis rate constant (mol L⁻¹ min⁻¹), K is the equilibrium adsorption coefficient (L mol⁻¹) and c is the reactant concentration (mol L⁻¹) at time t . At low substrate concentrations, the term Kc (Equation (2)) in the denominator can be neglected with respect to unity and the reaction kinetics exhibit first-order behaviour, i.e. $r = kKc$. This kinetic equation may be written in the integral form:

$$\ln\left(\frac{c_0}{c}\right) = kKt = k_{app}t \quad (3)$$

where c_0 is the initial reactant concentration (mol L⁻¹) and k_{app} is the apparent photocatalysis rate constant (min⁻¹) of the pseudo-first-order reaction. For convenient comparison of the

photocatalytic activity of the different thin films, k_{app} has been chosen as the appropriate kinetic parameter, since it enables the determination of photocatalytic activity independent of the previous adsorption period in the dark.³⁶

The photocatalytic activity of doped TiO₂ films was examined by the decomposition test of Rhodamine B (RhB). The degradation process, involving hydroxyl radical formation and subsequent degradation of RhB by the OH·, obeys apparent first-order kinetics.³⁷ The apparent rate constants (k_{app}) of RhB ($R^2 \geq 0.99$), obtained from the slopes (Equation (3)), and conversions (x) of RhB, are reported in Table 1. The TiO₂ films, pure and also doped, as prepared have effectively decomposed the RhB and the conversions were 19–61% (Table 1) after 90 min irradiation. It can be seen that after 90 min irradiation the RhB conversion on the pure TiO₂ film was not more than 41% and the apparent rate constant was 0.0074 min⁻¹. For TiO₂ films doped with Ag, Zr, and V, the conversion was enhanced significantly from 46 to 61%. The best apparent degradation rate constant (0.0125 min⁻¹), which was higher than that on the pure TiO₂ film by a factor of 1.7, was obtained on the Ag(3%)/TiO₂ photocatalyst. To compare the doping effect of Ag, Zr, and V acetylacetonate (%(w/w) metal/TiO₂) on the photocatalytic activity, the amount affording the maximum conversion was determined in all cases. The Ag(3%)/TiO₂, Zr(3%)/TiO₂, and V(5%)/TiO₂ samples showed the highest values (Table 1). The photodecomposition rate could be enhanced because more charge carriers are available. According to the principle of photocatalysis, in the V, Zr, and Ag-doped TiO₂ films metal can provide a shallow trap for the photogenerated electron and hole inhibiting recombination and extending the lifetime of the charge carrier. Chao *et al.*³⁸ found that Ag-doping promotes the anatase to rutile transformation, which is attributed to the increase in the specific surface area and enhances the electron–hole pair separation.

Some dopants can affect negatively the photoreactivity of TiO₂ (Table 1; Fe, Ni, Co, Mn, and Cr), changing the number of active sites, the surface group type or the acid-base properties.⁵ The different behaviour of the various samples is also related to the solubility of the transition metal in the support, which depends on the ion radius and charge.⁵ In this study, chromium was found to be the worst dopant among the various metals investigated (Table 1, conversion 21%). It has low diffusion length and also serves as a trap for the electrons produced under irradiation. The photocatalytic activity (RhB decomposition) of doped TiO₂ was greatly enhanced by incorporating it with V, Zr, and Ag. Therefore, mercury EDLs were then coated with a thin film of these doped titania samples and used for the photocatalysis of mono-chloroacetic acid (MCAA) in a MW field. Figure 5 shows the increase in chloride ion concentration in an aqueous solution in the presence of V, Zr, and Ag-doped TiO₂ under light irradiation (EDL emission lines: 365, 405, and 436 nm). Obviously, the photocatalytic activity of Ag(3%)/TiO₂ (Fig. 5, open triangle) was superior for the decomposition of MCAA in a MW field to that of the undoped counterpart.

We also investigated the effect of doping amount of vanadyl acetylacetonate on the photocatalytic activity of V(3%)/TiO₂ (1.167 at.%). When the doping level surpasses the optimum, which usually lies at a very low dopant concentration and low visible light absorbance, dopants become recombination sites and have adverse effects on photocatalysis.³⁹ We have found that the other two doped TiO₂ catalysts (1 and 5%) with different amounts of vanadium possessed similar morphologies (0.459 and 1.778 at.%) and showed different photocatalytic activities for the MCAA degradation (Fig. 6). The vanadium percentage (at.%) was

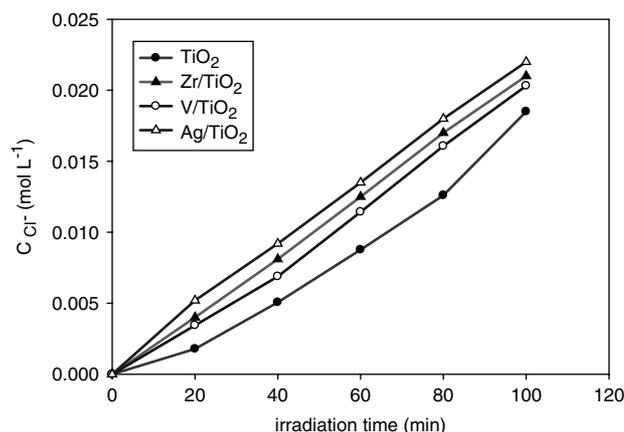


Figure 5. Effect of pure and Zr, V, and Ag-doped TiO₂ on the photocatalytic decomposition of MCAA (EDL intensity: 5.56 μW cm⁻²; EDL: two layers).

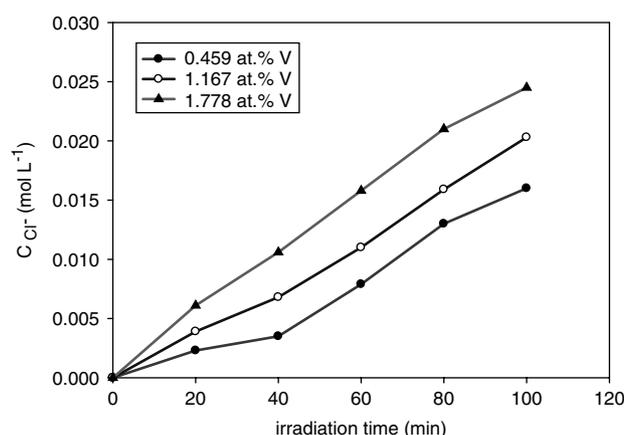


Figure 6. Effect of vanadium amount on the MCAA photocatalytic efficiency of doped TiO₂ (EDL intensity: 5.56 μW cm⁻²; EDL: two layers).

evaluated by XPS. The best degradation ability was obtained in the V(5%)/TiO₂ photocatalyst (Fig. 6, solid triangle). Higher amounts of vanadium may lead to the formation of new active sites, which are also responsible for the observed higher photocatalytic activity.

CONCLUSION

Pure and transition metals doped TiO₂ thin films have been prepared by the sol–gel process. Only the anatase phase was found in the Raman spectra recorded. EDLs were coated by doped TiO₂ in the form of the thin films. The degradation efficiency of doped TiO₂ films was examined by the decomposition of Rhodamine B and by MCAA degradation to HCl, CO₂, and H₂O in a MW field. It has been found that with a suitable amount of V, Zr, and Ag showing significant absorption in the visible region, the metal dopants effectively increase the photocatalytic activity of the TiO₂ film on the EDLs. The best apparent degradation rate constant (0.0125 min⁻¹), which was higher than that on the pure TiO₂ film by a factor of 1.7, was obtained on the Ag(3%)/TiO₂ photocatalyst. The doping amount effect of vanadium acetylacetonate on the photocatalytic efficiency of V-doped TiO₂ has been determined.

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